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Research Article

Homologous Series of Chemical Compounds in Three-component Systems ($A^{a+} – B^{b+} – C^{c-}$) and (Zn^{2+} - Ge^{4+} - P^{3-}) in Generalized Form

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Abstract

For the first time, a method for calculating formulas of homologous series of chemical compounds of the systems ($A^{a+} – B^{b+} – C^{c-}$) and {$Zn^{2+} – Ge^{4+} – P^{3-}$} in a generalized form is presented. The calculation is confirmed by the literature experimentally obtained compounds: thirteen compounds of the system ($Na^{+} – Ti^{4+} – O^{2-}$), seven – systems ($Li^{+} – Ti^{4+} – O^{2-}$), five – systems ($K^{+} – V^{5+} – O^{2-}$), eight – systems ($Ba^{2+} – Cu^{2+} – O^{2-}$). Homological series in ($A^{a+} – B^{b+} – C^{c-}$) have the following generalized form: $A_{\{t-k\cdot r+nr-r\}bc}B_{rac}C_{\{t-k\cdot r+nr\}ab}$ and $A_{tbc}B_{\{r-k\cdot t+nt-t\}ac}C_{(r-k\cdot t+nt)ab}$.

In ($Zn^{2+} – Ge^{4+} – P^{3-}$) systems for the *m*-group the formulas of homologous series, that develops towards Ge_3P_4, have the following generalized form: $Zn_{6t}Ge_{(6r-6kt+6n-6t)}P_{(8r-8kt+8n)}$ and for αm-homologous series – $Zn_6Ge_{3n}P_{4(n+1)}$. A method for calculating formulas of homologous series of chemical compounds in a generalized form can be used for any system of chemical elements.

INTRODUCTION

The search for new Chemical Compounds (CC) in multicomponent systems of Chemical Elements (CE) is a difficult task. The great variety of properties of a set of Three-Component Chemical Compounds (TCC) is of great interest in solving a number of scientific and applied studies. There are known works in the literature that use the mathematical apparatus for predicting phases in multicomponent systems. Thus, semiempirical quantum-chemical methods, such as Hartree-Fock-Rutaan and Hartree-Fock-Slater methods [1-3], are used to calculate the formulae of hypothetical multicomponent CC. When using these methods to describe a chemical system, many physical and chemical phenomena must be taken into account. The exact solution of the basic laws leads to overcomplicated calculations. Therefore, for practically all CE systems, the solution of the corresponding electronic equations used in quantum-chemical calculations is only possible approximately. Well-known quantum-chemical methods of calculation, allow to calculate the formula of any CC, are rather complicated and require special knowledge in the field of mathematical programming.

According to the works [4-7], knowledge of the laws of formation of Homological Series (HS) of chemical compounds can be included in the process of searching for new CC.

Thus, the author of the work [8, p. 190] believes that "...the activated complex theory consists in the fact that in the course of any chemical reaction, the initial configuration of atoms passes to the final one as a result of continuous change of interatomic distances", which is characterized by the formation of various critical intermediate configurations, i.e. activated complexes". On the basis of this idea, in the works [4-7] the method of calculation of formulae of HS of chemical compounds of three-component systems of CE ions was developed.

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It is known [9,10] that multicomponent CE systems include CC, which are combined into different HS. As the HS develops, the fundamental properties of its members change in a regular way, which is determined by a regular change in the crystal structure of homologs [8-10]. In turn, the regular change in the crystal structure of homologs is determined by the regular change in their composition, which contributes to the search for new CC in [4-7]. In the works [9-11], the structural homology of inorganic CC of different systems of CE is discussed in detail.

So far, judging from the literature, the formulas of HS are known, which were obtained only empirically.

In the literature, there are known HS of systems with a single set of chemical elements:

$Ba_mCu^{2+}_{m+n}O$ [12]; or $La_nNi_nO_{3n-1}$ [13]; $La_{n+1}Ni_nO_{3n+1}$, n = 1-5 [14]; $La_{n+1}Ni_nO_{3n-1}$, n = 7, 9, 13 and 30 [15]; $La_{2n-4}Ni_2O_{4n-5}$, n = 5-8 [16]; or $Fe^{2+}nFe^{3+}_{2m}O_{n+3m}$ [17] or $Sr_{n+1}Ti_nO_{3n+1}$[18]. Thus, in the (Ba^{2+} – Cu^{2+} – O^{2-}) system, the homologous series of CC is described by the formula $Ba_mCu_{m+n}O_{3n-1}$, where 2m = 2n – 1 [12], and in [17] it is reported that a series of CC belonging to the HS were obtained, described by the formula $nFeO{\cdot}mFe_2O_3 \equiv Fe^{2+}_nFe^{3+}_{2m}O^{2-}_{n+3m}$.

Additionally, experimentally obtained inorganic CC described by formulas that exhibit regular changes in composition are known in the literature: M_nO_{3n-1} (M = Mo, W) [19], M_nO_{2n-1} (M = Ti, V) (n = 4-10) [20-24], W_nO_{3n-2} (n = 20, 38-40) [24].

However, in the case of “Magneli phases” in the systems (M – O), where M ≡ Mo, W, V, Ti, [19-24] and in the system (La – Ni – O) [13-16], all these formulas, without taking into account the existence of atom of metal with the same name with different atom valence in them, in our opinion, they cannot be considered correct. Following the electron neutrality of CC formulas, in all crystal lattices of CC belonging to the “Magnéli phases” described by formulas from [19-24], two metal ions of the same name with different atom valence should be present: for example, M^{5+} and M^{6+} in Me_nO_{3n-1} or in W_nO_{3n-2} (M ≡ Mo, W), or M^{3+} and M^{4+} in M_nO_{2n-1} (M ≡ Ti, V). In the formulas described in [13-16] two ions Ni^{2+} and Ni^{3+} with different atom valence should be present as equal chemical entities, determining the existence of the crystal lattice of CC. That is why the formulas of “Magnéli phases” from [19-24], in our opinion, should be attributed not to two-component, but to three-component CE systems. In turn, the formulas related to the (La – Ni – O) system [16-19] belong not to a three-component system but to a four-component CE system, (La^{3+} – Ni^{2+} – Ni^{3+}). For this reason, the formulas from [19-24], in our opinion, could be written as follows:

$Me_nO_{3n-1} \equiv Me^{5+}_2Me^{6+}_{n-2}O_{3n-1}$, where (Me ≡ Mo, W) and n = 8–12, 14 [19]; or $Me_nO_{2n-1} \equiv Me^{3+}_2Me^{4+}_{n-2}O_{2n-1}$, where (Me ≡ Ti, V) and n = 4-10 [20-24]; or $W_nO_{3n-2} \equiv W^{5+}_4W^{6+}_{n-4}O_{3n-2}$, where n = 20, 38-40 [24], and the formulas from [13-16] are suggested to be written as follows: $La_nNi_nO_{3n-1}$ [13] $\equiv La_nNi^{2+}_2Ni^{3+}_{n-2}O_{3n-1}$, $La_{n+1}Ni_nO_{3n+1}$ [14] $\equiv La_{n+1}Ni^{2+}Ni^{3+}_{n-1}O_{3n+1}$, $La_{n+1}Ni_nO_{3n-1}$ [15] $\equiv La_{n+1}Ni^{2+}Ni^{3+}_{n-1}O_{3n-1}$ and $La_{2n-4}Ni_nO_{4n-5}$ [16] $\equiv La_{2n-4}Ni^{2+}_{n-2}Ni^{3+}_2O_{4n-5}$.

In the literature, for the system (M^+ – Ti^{4+} – O^{2-}), where $M^+ \equiv Li^+$, Na^+, K^+, Rb^+, Cs^+, a series of formulas for experimentally obtained TCC is known, generalized for n = 1-9 in the form of $M^+_4Ti^{4+}_nO_{2(n+1)}$ [24].

The aim of this study is to develop a method for calculating the formulas of a homologous series of three-component systems of chemical elements in a generalized form using the geometric features of the triangle representing the system of chemical element ions.

Justification of the method for calculating homologous series of chemical compounds

The method for calculating HS of three-component systems developed in [4-7] allows, in our opinion, for the generalized determination of HS formulas. This conclusion is drawn from the findings presented in [6,7], which provide numerous confirmations of the accuracy of the HS calculation method for a range of three-component systems through experimental results taken from the literature. It should be noted, however, that the laws governing the formation of individual CC and the laws governing the formation of HS are different. Before the publications of [4-7], there was no possibility in the literature to predict the formation scheme of HS. In some cases, HS formulas were only experimentally determined in works [13-24].

Based on the works [4-7], the justification for the generalized method of calculating HS can be formulated as follows:

1) In our view, the rule (or scheme) for forming HS of chemical compounds can be formulated by considering all possible directions of chemical interactions between the components of the system, as allowed by the combination of the valence electron count of chemical elements and the composition of complex atomic clusters in the system. In reality, only ions of elementary substances and “certain intermediate atom configurations critical for a given reaction” participate in chemical interactions [8]. In our case, these are activated CC and charge clusters (ChCl). It is clear that determining the formula of HS is possible if, among the many presumed directions of chemical interaction between the components of the CE system, we can select those responsible for the formation of HS. Therefore, to

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solve this problem, the CE system must be represented as ions, as only ions can chemically interact with each other, producing intermediate, more complex, compositionally charged clusters and activated multi-component CC. To do this, the system is represented as a triangle (Figures 1-3), with CE ions placed at its vertices.

2) It was found that the geometric features of the triangle representing the system of CE ions consist of representing the reaction of the interaction between any pair of reacting system components as a line segment, where each pair of reactants and the product of their interaction lie on a line segment unique to them. In cases where line segments connecting different pairs of chemically interacting system components intersect at a single point, the common product of the interaction, ChCl or activated CC, must be located at that point. This feature is explained by the difference in the laws governing the interaction of different pairs of reactants, which are determined by the different combinations of valence ions of CE and the composition of interacting pairs of reactants represented by different line segments: at the point of intersection of these line segments, different laws of chemical interaction of different pairs of chemical entities cannot coexist simultaneously.

Thus, the calculation of HS formulas, i.e., the search for new HS homologs, is based on the premise that homologs are located within a triangle at the intersection of line segments connecting different pairs of chemically interacting components of the system, including ions, CC and ChCl.

3) Next, we will consider that homologs enriched with the two-component CC (TwCC), A_cC_a, belong to the *p*-groups of HS, while homologs enriched with the B_cC_b cluster belong to the *m*-groups of HS – Figure 1-3. HS are formed depending on the direction of development through a chain of sequentially occurring interactions of TCC with cation A^{a+} – the development direction of *p*-groups of HS is A_cC_a. When TCC interacts with cation B^{b+} – the *m*-groups of HS develop towards B_cC_b.

The formation of HS involves three-component charge clusters ($TChCl_n$) through interaction with anion C^{c-} (Figures 1-3).

The formation of HS is described by the following scheme:

$$TChCl_{n=1} + C^{c-} \rightarrow TCC_{n=1},\ TCC_{n=1} + A^{a+}\ (\text{or } B^{b+}) \rightarrow TChCl_{n=2},\ TChCl_{n=2} + C^{c-} \rightarrow TCC_{n=2},\ TCC_{n=2} + A^{a+}\ (\text{or } B^{b+}) \rightarrow TChCl_{n=3},\ TChCl_{n=3} + C^{c-} \rightarrow TCC_{n=3} \quad (1)$$

In the text, the determined formulas of CC and ChCl as reactants and products of their interaction are highlighted in bold. The value of n is determined experimentally, where n represents the position of the homolog in HS, ($1 \le n$).

4) Activated TXC_n are located on line segments (A_cC_a – B_cC_b) – Figures 1-3. In works [4-6], the nature of the connection of the same TCC_n, which simultaneously belongs to both the *p*-groups and *m*-groups of HS, is described. Following the conditions outlined in paragraph 3 regarding the membership of TCC in *p*-groups and *m*-groups of HS, it can be concluded that in the case of *p*-groups of HS, its first homologs, $TCC_{n=1}$, are located on the line segment (p. 2 – B_cC_b), excluding B_cC_b, and the clusters $TCC_{n>1}$ are located on the line segment (p. 2 – A_cC_a), excluding point 2 and A_cC_a (Figures 1,2).

In the case where the same TCC_n cluster belongs to the *m*-group of HS, its first homologs, $TCC_{n=1}$, are located on the line segment (p. 2 – A_cC_a), excluding A_cC_a. The clusters $TCC_{n>1}$ are located on the line segment (p. 2 – B_cC_b), excluding p. 2 and B_cC_b (Figures 1,3).

5) Clusters $TChCl_{n=1}$, belonging to *p*-groups of HS, are located on the line segment (p. 1 – B^{b+}), excluding B^{b+}, and clusters $TChCl_{n>1}$ are located on the line segment (p, 1 – A_cC_a), excluding p. 1 and A_cC_a – Figures 1,2. In the text and in Figure 1, the following notations are used: p. 1 ≡ point 1, p. 2 ≡ point 2, p. 3 ≡ point 3, and so on.

In the case where the $TChCl_n$ cluster belongs to the *m*-group of HS, its first homologs, $TChCl_{n=1}$, are located on the line segment (p. 1 – A^{a+}), excluding A^{a+}, and clusters $TChCl_{n>1}$ are located on the line segment (p, 1 – B_cC_b), excluding p. 1 and B_cC_b (Figures 1,3).

6) TCC_n and $TChCl_n$, occupying the same position in the same HS, are linked by the reaction:

$$TChCl_n + C^{c-} \rightarrow TCC_n \quad (2)$$

7) Any known TCC is necessarily a member of some HS.

8) Any HS consists of a CC branch and a ChCl branch, the members of which are linked by reaction (2). Each branch of the same HS develops towards enrichment with only one Two-component CC (TwCC), either A_cC_a or B_cC_b.

9) The geometric features of the triangle, if following scheme (1), ensure a systematic and periodic The geometric features of the triangle, if following scheme (1), ensure a systematic and periodic change in the composition of homologs in HS.

10) The difference in compositions, Δ, of any adjacent homologs in the same HS is constant:

$$\Delta_{m(p)} = TCC_{n+1} - TCC_n = TChCl_{n+1} - TChCl_n \quad (3)$$

11) The charges of all ChCl in the same HS are identical.

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12) In the case of determining the formulas of HS to which some known (basic) $TCC_{n(bas)}$ belongs, the calculation of HS formulas is carried out as follows: first, the formulas of $TChCl_{n(bas)}$, $TCC_{n(bas)+1}$, and $TChCl_{n(bas)+1}$ are calculated, then the formulas of Δ and the first terms, $TCC_{n=1}$ and $TChCl_{n=1}$, of the considered HS are determined. Formulas $TCC_{n=1}$ and $TChCl_{n=1}$ are calculated by subtracting the maximum number of times the formula $\Delta_{m(p)}$ from the formulas of basic clusters while retaining the minimum number of the cation contained in the formula $\Delta_{m(p)}$ in their composition:

$$TCC_{n(bas)} - k\cdot\Delta_{m(p)} = TCC_{n=1} \quad (4)$$

$$TChCl_{n(bas)} - k\cdot\Delta_{m(p)} = TChCl_{n=1} \quad (5)$$

where ($0 \le k$). If $k = 0$, then n(bas) = 1.

13) The formula of any homolog in the same HS, i.e., the formula of the HS, is determined as follows:

$$\text{CC branch: } TCC_{n=1} + (n-1)\cdot\Delta_{m(p)} = TCC_n \quad (6)$$

$$\text{ChCl branch: } TChCl_{n=1} + (n-1)\cdot\Delta_{m(p)} = TChCl_n \quad (7)$$

14) When calculating HS, it should be taken into account that one of the CE may have different valencies, being not only a component that does not introduce impurities into the crystalline lattice of TCC but also one of the main CE in the crystalline lattice.

In practice, researchers often need to determine the formulas of HS to which a known $TCC_{n(bas)}$ already belongs. In the formation of these HS, any TCC_n can participate, including $TCC_{n=1}$ and $TCC_{n>1}$.

Calculation of homologous series in the ($A^{a+} - B^{b+} - C^{c-}$) system

Let's examine the sequentially occurring chemical reactions in a three-component system. The formation of HS occurs according to scheme (1). The system ($A^{a+} - B^{b+} - C^{c-}$) is initially in a state where the interaction of a positively charged ion with an anion will lead to the formation of activated TwCC, A_cC_a, and B_cC_b (Figure 1).

$$cA^{a+} + aC^{c-} = A_cC_a \quad (8)$$

$$cB^{b+} + bC^{c-} = B_cC_b \quad (9)$$

Activated TwCC, A_cC_a and B_cC_b can interact with each other to form TCC_n based on the ratios of ions A^{a+}, B^{b+} and C^{c-} in TCC_n based on the ratios of ions A^{a+}, B^{b+} and C^{c-} in $TChCl_n$, which participate in reaction (2):

$$x\cdot A_cC_a + y\cdot B_cC_b = (A_{xc}B_{yc}C_{(x+y)ab} = TCC_n)o \quad (10)$$

Furthermore, according to the initial ratios of ions in TCC_n and $TChCl_n$, the interaction of positively charged ions with each other leads to the formation of two-component charged clusters ($TwChCl_n$), which are connected to TCC_n and $TChCl_n$ by reaction (2), where ($1 \le n$):

$$x\cdot A^{a+} + y\cdot B^{b+} = ([A_{xb}B_{ya}]^{(x+y)ab+} = TwChCl_n) \quad (11)$$

The combined interaction of ($TChCl_{n=1}$ = p. 1) and $TwChCl_{n=1}$ with anion C^{c-} according to (2), as well as activated A_cC_a and B_cC_b with each other leads to the formation of a cluster of ($TCC_{n=1}$ = p. 1) – Figure 1. Thus, the clusters ($TChCl_{n=1}$ = p. 1), ($TwChCl_{n=1}$ = p. 3) and ($TCC_{n=1}$ = p. 2) turn out to be the founders of two groups of HS, *am*-group and *ap*-group, since ($TChCl_{n=1}$ = p. 1) and ($TCC_{n=1}$ = p. 2) can interact with both B^{b+} and A^{a+}, respectively. The interactions mentioned are characterized by the intersection of segments corresponding to the reacting components of the CE system. Thus, the formation of different clusters $TChCl_n$ are characterized by the intersection of segments ($A_cC_a - B^{b+}$) and ($B_cC_b - A^{a+}$), and the formation of cluster TCC_n is characterized by the intersection of segments ($TChCl_n - C^{c-}$), ($A^{a+} - B^{b+}$) and ($A_cC_a - B_cC_b$), which is described by the following reaction equations in the formation of the *am*-group of HS and *ap*-group of HS (Figure 1).

$$bA_cC_a + acB^{b+} = aB_cC_b + bA^{a+} = ([A_{bc}B_{ac}C_{ab}]^{abc+} = TChCl_{n=1} = \text{p. 1}) \quad (12)$$

$$([A_{bc}B_{ac}C_{ab}]^{abc+} = TChCl_{n=1} = \text{p. 1}) + abC^{c-} = \{bcA^{a+} + acB^{b+} = ([A_{bc}B_{ac}]^{2abc+} = TwChCl_{n=1} = \text{p. 3}) + 2abC^{c-} = bA_cC_a + aB_cC_b = (A_{bc}B_{ac}C_{2ab} = TCC_{n=1} = \text{p. 2}) \quad (13)$$

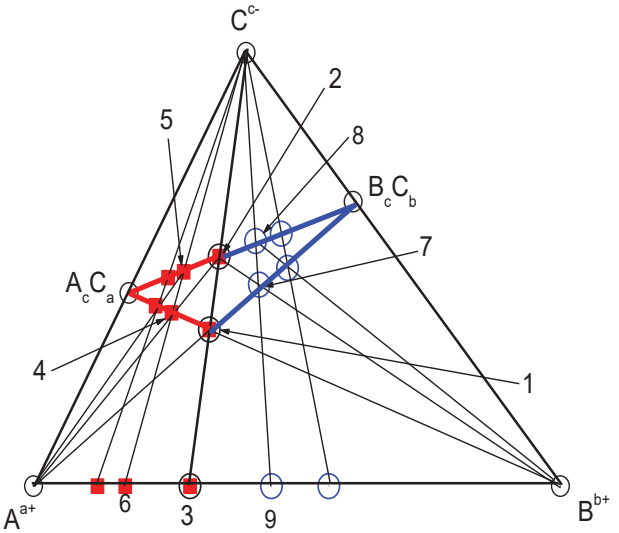

Figure 1: System ($A^{a+} - B^{b+} - C^{c-}$): *ap*-HS (A_cC_a direction) and *am*-HS (B_cC_b direction).
ap-HS: (p. 1 = $TChCl_{n(bas)=1} = [A_{bc}B_{ac}C_{ab}]^{abc+}$), (p. 2 = $TCC_{n(bas)=1} = A_{bc}B_{ac}C_{2ab}$) (p. 3 = $TwChCl_{n(bas)=1} = [A_{bc}B_{ac}]^{2abc+}$), (p. 4 = $TChCl_{n=2} = [A_{2bc}B_{ac}C_{2ab}]^{abc+}$), (p. 5 = $TCC_{n=2} = A_{2bc}B_{ac}C_{3ab}$, (p. 6 = $TwChCl_{n=2} = [A_{2bc}B_{ac}]^{3abc+}$);
***am*-HS**: (p. 1 = $TChCl_{n(bas)=1} = [A_{bc}B_{ac}C_{ab}]^{abc+}$), (p. 2 = $TCC_{n(bas)=1} = A_{bc}B_{ac}C_{2ab}$), (p. 3 = $TwChCl_{n(bas)=1} = [A_{bc}B_{ac}]^{2abc+}$), (p. 7 = $TChCl_{n=2} = [A_{bc}B_{2ac}C_{2ab}]^{abc+}$), (p. 8 = $TCC_{n=2} = A_{bc}B_{2ac}C_{3ab}$, (p. 9 = $TwChCl_{n=2} = [A_{bc}B_{2ac}]^{3abc+}$).